Damage-Free Sample Preparation of Carbon Phosphonitride for High Resolution Transmission Electron Microscopy

Haw-Tyng Huang[1], Qianqian Wang[3], Stephen J. Juhl[2], Arani Biswas[2], Missy Hazen[4], Nasim Alem[1], John V. Badding[1,2], Timothy A. Strobel[3]

[1]*Department of Materials Science and Engineering, Pennsylvania State University, University Park, PA, USA*
[2]*Department of Chemistry, Pennsylvania State University, University Park, PA, USA*
[3]*Geophysical Laboratory, Carnegie Institution of Washington, Washington, DC, USA*
[4]*Huck Institutes of the Life Sciences Microscope Facilities, Pennsylvania State University, University Park, PA, USA*

Carbon phosphonitrides are a new class of 3D carbon nitride network with extreme P doping. Phosphorus doped g-C_3N_4 shows reduced bandgap and higher electrical conductivity while retaining its layered structure. [1] Recent advances in the synthesis of P-doped carbon nitride report that thermally polymerized $P(CN)_3$ precursors form an extended carbon phosphonitride network.[2] Such carbon phosphonitride has an extremely high phosphorus to nitrogen ratio (P:N = 1:3) and is expected to be a narrow gap semiconductor. Since the local structure and bonding of the material is critical for determining the electronic and optoelectronic properties, high-resolution transmission electron microscopy (HRTEM) is an important probe in order to understand the structure-property relationship. Preparing a thin specimen of such light-element materials for HRTEM remains a challenge due to their sensitivity for ion-milling artifacts. Furthermore, in such ternary light-element systems, the focused ion beam (FIB) preparation process often causes changes in chemical composition and bonding. [3] In the present case, we found it difficult to make a homogeneous thickness sample because of the preferential sputtering effect in the FIB (Figure 1).

In this work, we discuss methods and conditions for preparing TEM specimens of carbon phosphonitride using ultramicrotomy as a damage-free technique. In all cases TEM specimens were encapsulated in epoxy and sectioned by a Diatome Ultra 45-degree diamond knife. Sections of carbon phosphonitride with thickness of 70 to 90 nm were obtained by room-temperature ultramicrotomy, which were demonstrated to achieve the electron transparency required for high-resolution imaging (Figure 2). A FIB specimen prepared with a Ga+ ion beam is also presented for comparison (Figure 1). TEM images of the FIB specimen show the curtaining effect, which is derived from the channeling of the high-energy ion beam. The HRTEM image in Figure 1b further demonstrates the irregular thickness across the sample and preferential sputtering of the carbon-rich amorphous matrix. In contrast, the scanning transmission electron microscopy (STEM) image of the microtomy specimen (Figure 2a) exhibits no artifacts derived from the sample preparation process. Moreover, the HRTEM image (Figure 2b) shows homogeneous thickness across different domains in the specimen. In the microtomy sample, the diffraction contrast dominates in the HRTEM image as opposed to thickness contrast, which creates no ambiguity and is ideal for crystallographic analysis.

References:

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[3] N. D. Bassim *et al*, J. Microsc. **245** (2012), 288-301.

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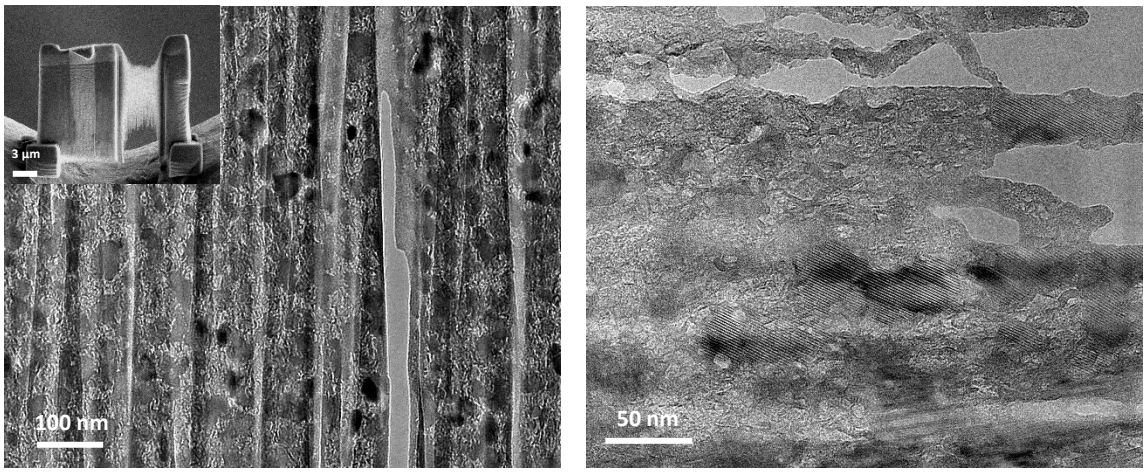

Figure 1. (A) A low-magnification TEM image from a FIB specimen prepared with 2kV Ga^+ final thinning shows significant curtaining effect. The preferential sputtering effect of the amorphous domains over the crystalline domains is further demonstrated in (B) the HRTEM image, which shows significant thickness contrast in the crystalline regions.

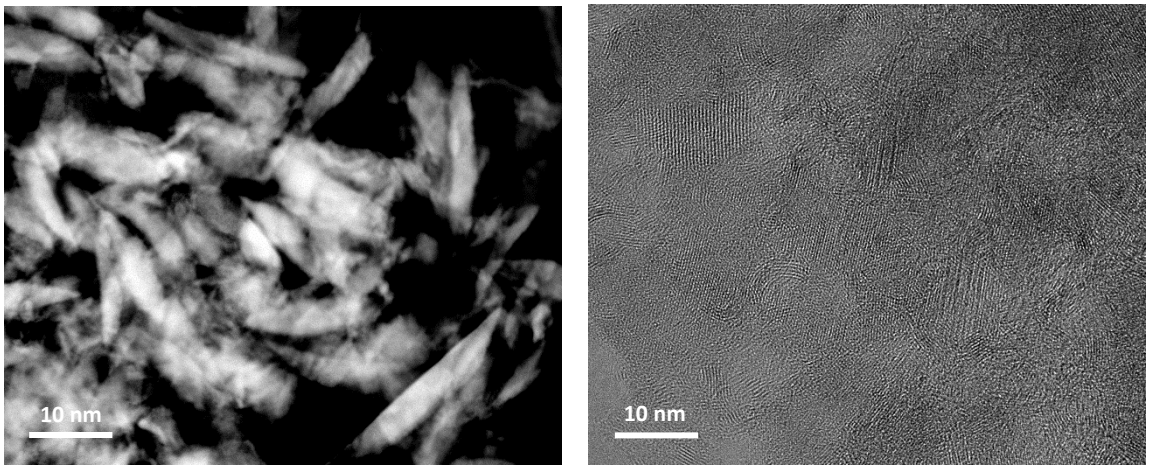

Figure 2. (A) A STEM image from a specimen prepared by ultramicrotomy shows the typical morphology of the carbon phosphonitride sample on TEM grids. The thickness contrast is not observed in these microtomy specimen as shown in (B) the HRTEM image in spite of the presence of multiple crystalline and amorphous domains.